

Applications with the Dedicated Polymer Scanning Transmission X-ray Microscope at ALS Beamline 5.3.2

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H. ADE,^{1*} A. P. HITCHCOCK,² G. E. MITCHELL,³ A. L. D. KILCOYNE,¹
T. TYLISZCZAK,⁴ R. FINK,⁵ AND T. WARWICK⁴

¹Department of Physics, North Carolina State University, Raleigh, North Carolina 27695, USA

²Brockhouse Institute of Materials Research, McMaster University, Hamilton, Ontario, L8S 4M1, Canada

³Dow Chemical, 1897 Bldg., Midland, MI 48667, USA

⁴Lawrence Berkeley National Laboratory, Berkeley, California 94720, USA

⁵University of Erlangen, Physikalische Chemie II, 91058 Erlangen, Germany

The Polymer Scanning Transmission X-ray Microscope at beam line 5.3.2 (5.3.2 STXM) had been conceived in 1997, and was implemented in the last few years by a consortium of researchers from NCSU, McMaster, Dow Chemical, and the ALS [1]. The "application-specific design," optimized for use over the 280 to 560 eV energy range, has resulted in an instrument at a dedicated beamline that provides easy use and access for such instrumentation. Essentially all applications at this facility make use of Near Edge X-ray Absorption Fine Structure Spectroscopy (NEXAFS) to obtain improved contrast and/or derive quantitative compositional or orientational information. Recent reviews of NEXAFS microscopy of organic materials provide a context [2,3].

The productivity of the Polymer STXM has been due, in part, to the continuously available and relatively stable beam delivered by the high brightness bending magnet at 5.3.2 [4]. The beamline allows trade-off between flux and energy resolution and/or spatial resolution, directly controllable by the user and easily adjusted via slits. The implementation of differential laser interferometry in an active feedback loop to precisely control the relative sample and zone plate (ZP) positions in the microscope provides reproducible measurements.

In addition, the laser interferometer allows dynamical suppression of vibrations. The position of the microscope relative to the photon beam has not changed after more than a year of continuous use. Only minor adjustments to mirrors mounted on the sample and ZP stages of the instrument are required when maintenance procedures are undertaken. Presently, ZPs that have an outermost zone width of 35 nm are utilized. Periodic features with <25 nm half-period can be resolved with 5–10% contrast with relatively short acquisition times and a resolving power >3000. (An example of the spatial resolution achieved is shown in the article by Warwick et al. in this issue that describes the sister STXM at ALS beamline 11.0 [5].) Use of 25 nm ZPs is anticipated in the near future, further improving the spatial resolution. To enhance the utility of the 5.3.2 STXM, a number of sample manipulation tools are in preparation including in-situ sample annealing. Details about the beamline and the instrument can be found in recent publications by Kilcoyne et al. [1] and Warwick et al. [4]. We focus our attention in this article on short descriptions of applications in the hope that these inspire other researchers to utilize the 5.3.2 STXM and related ALS facilities. A portion of the beamtime at 5.3.2 is available

through the peer-reviewed General User process administered by the ALS.

Applications

Polymer-clay nanocomposites. Organic-inorganic nano-composites are a very promising class of materials under active investigation. In these materials one can, through nanoscale engineering, combine the flexibility of polymers with beneficial properties of the inorganic component and thus produce a new class of lightweight materials. A team of researchers from SUNY@Stony Brook, NCSU, EXXON, and UNC-Chapel Hill explored the efficacy of combining polymer blending with clay-homopolymer composite methods in order to overcome some of the fundamental problems inherent in the two technologies when used separately [6]. Experiments show that high aspect ratio inorganic fillers, with at least one dimension in the nanometer range, can form in-situ grafts by adsorbing large amounts of polymer. These graft composite nano-structures in turn are very effective at reducing the interfacial tension in highly immiscible blends and are thus inducing compatibilization. This phenomenon should be widely applicable to most polymer blends. A variety of model materials primarily based on polystyrene (PS),

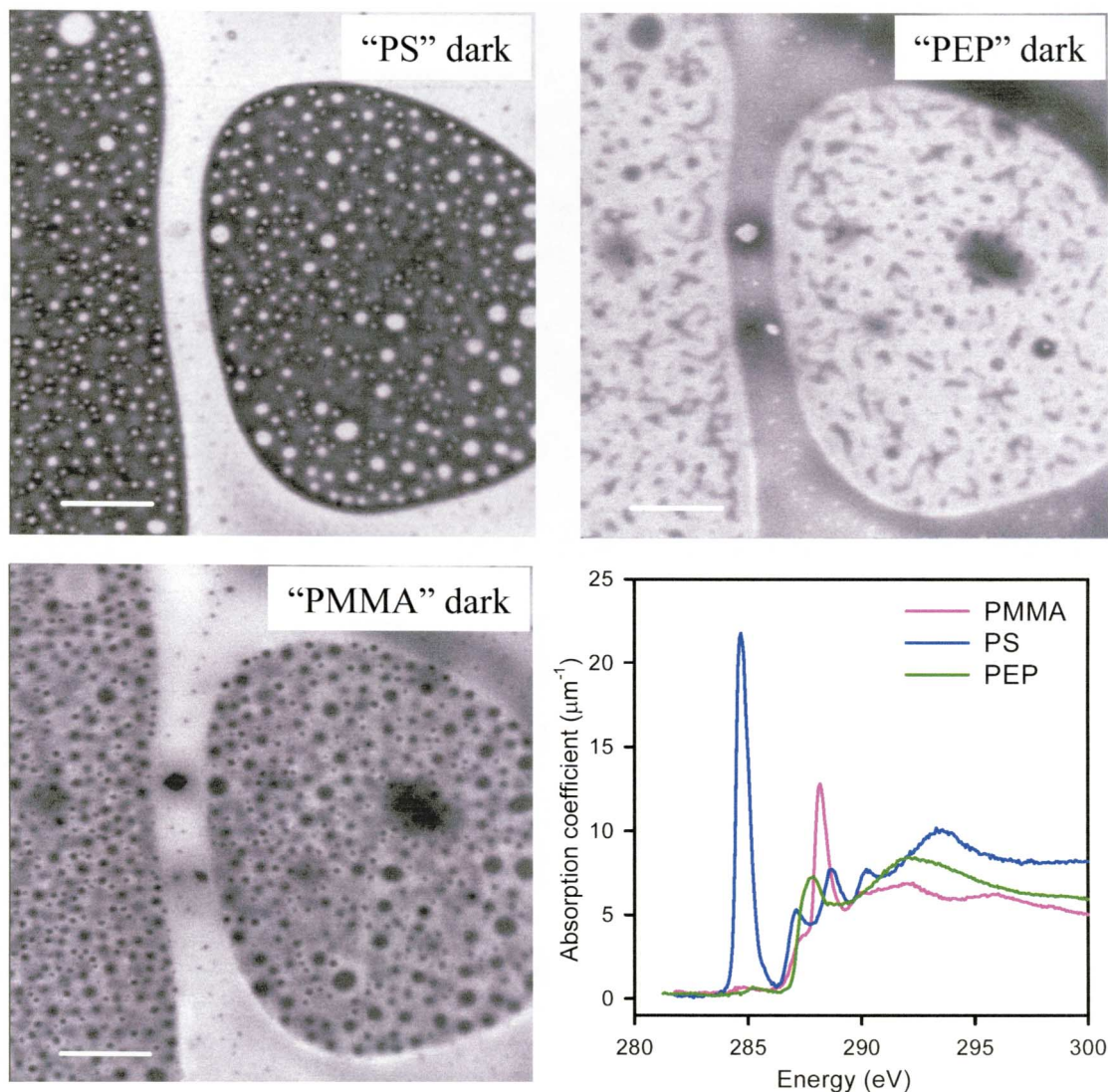


Figure 1: 30 x 30 micron images of PS/PMMA/PEP tertiary polymer thin film blend without clay imaged at (a) 285.15 eV, (b) 287.6 eV, and (c) 288.4 eV, respectively, to emphasize and delineate the components.

polymethyl methacrylate (PMMA), and polyethylene-propylene (PEP) have been prepared and investigated with the 5.3.2 Polymer STXM and complementary characterization tools [6].

Characterizing PS/PMMA/PEP thin film blends prepared with and without various alkane functionalized montmorillonite clays reveal that the morphologies in the presence of the clay exhibit much smaller domains, often

near the resolution limit of the 5.3.2 Polymer STXM. In contrast, blends without clays have domains many microns in size. The mechanism by which the clay is facilitating the compatibilization of the polymers has been elucidated in additional experiments. The imaging properties of the 5.3.2 Polymer STXM are particularly helpful in differentiating components in this ternary system (see Figure 1) and in quantifying the level of mixing. These experi-

ments have shown that alkane-modified montmorillonite clays can be effective compatibilizers of incompatible polymer blends. This opens the door to a new, simple, and cheap process to produce novel inorganic-organic nano-composites.

Chemical mapping of core-shell microspheres and microcapsules. Harald Stöver's group at McMaster University is developing

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new methods to prepare polymer microspheres and microcapsules for use as separation media, solid state support, and/or controlled delivery of agricultural and health care compounds [7]. Polymer STXM allows powerful chemical speciation at the required length scale, which helps improve materials properties and processing by providing detailed information on the actual as compared to the hypothesized distribution of chemical components. There is considerable interest in using polymer microcapsules for chemical storage and controlled delivery. Applications include insect control through mate-attraction pheromones and controlled drug delivery. Novel composite capsules are fabricated as follows. First, structured microspheres are formed through interfacial polyaddition between isocyanates dissolved in

the organic core-phase, and aqueous polyamines. The microspheres consist of 55%-divinyl, monovinyl benzene (DVB-55) and have 40% total pore volume with a maximum pore diameter of about 5 nanometer. They are surface-functionalized by reacting the residual vinyl groups with maleic acid to form grafted succinic acid groups. The microspheres are then added to the core phase, and are given a high surface polarity to ensure that they self-assemble at the oil-water interface and become embedded across the dense outer polyurea skin (Figure 2). In this system the mechanical and release properties are provided separately by the strong and dense polyurea wall, and by embedded porous microspheres, respectively. This approach offers improved control of total release rate through control over the amount of

embedded microspheres. STXM was used to map the location and concentration of the succinic acid, as well as to detect whether polyurea would form within the pores of the microspheres, potentially blocking through-pore release. For this study, capsules were embedded in an improved epoxy resin developed for STXM that is based on aliphatic epoxy components and is hence free of aromatic and carbonyl groups. This new resin allowed quantitative mapping of the aromatic DVB55 microspheres, the polyurea, and the succinic acid shell (Figure 2), without interference from chemical signals of the epoxy resin. The microspheres are embedded across the dense outer polyurea layer, and the succinic acid linker is concentrated at the microsphere surface. However, the STXM results also indicate

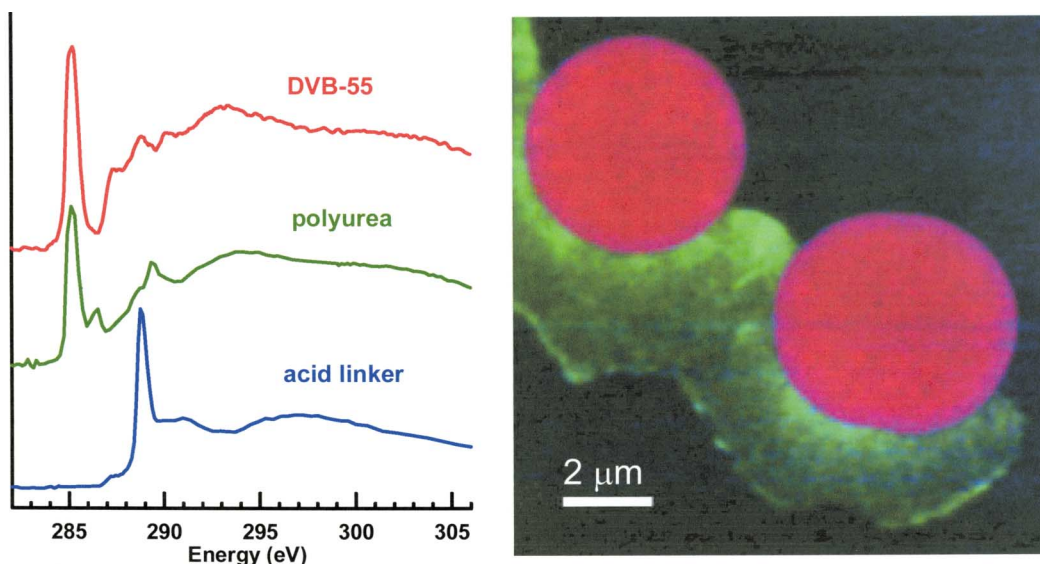


Figure 2: Chemical maps of the DVB-55, polyurea, and succinic acid components of composite capsules derived by fitting a C 1s image sequence to the indicated spectra.

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that dense polyurea regions form underneath the microspheres, suggesting that water and/or amine may penetrate through the porous microspheres, or be attracted to the very polar succinic acid layer, during capsule formation. Hence, other non-ionic polar additives may need to be explored in order to reduce the polyurea skin density underneath the microspheres. Finally, it appears that polyurea is excluded from the pores of the DVB particles. This agrees well with gravimetric measurements of fill release, which indicate that release scales with microsphere loading.

Growth and morphology of organic thin films. Organic thin films have attracted attention for a number of reasons, including the possibility of producing cheap and large-scale electronic devices. Organic light emitting devices (OLEDs) are already produced and there is an increasing interest in producing organic field effect transistors (OFETs). High charge carrier mobilities are an important prerequisite for ultimate device performance and thus the structural properties of the organic films have to be optimized. The growth mechanisms of

large organic molecules on primarily metal substrates have been studied previously. In order to operate an OFET, the gate electrode must be insulated from the electrically active material and therefore, growth of organic films on insulators are preferable to metals. To study the morphology and molecular orientation of organic films on insulators, a team from Würzburg, Erlangen, and NCSU has investigated thin films of TCNQ and Cu(TCNQ)₂ grown on Si₃N₄ [8]. TCNQ is one of the molecular components of the first organic superconductor TTF-TCNQ and is known to form metal-organic radical anion charge transfer complexes allowing field-induced bistable electric switching.

Figure 3 shows a typical image of vacuum sublimated, nominally 80 nm thick films prepared by co-evaporation of TCNQ and Cu onto Si₃N₄ membranes. Structures with a diameter of up to 40 μm and mainly two different grey shades were observed. The dendritic growth indicates diffusion-limited growth and results in structural inhomogeneities. Microspectroscopic analysis of the different areas reveals that the brighter areas consist of Cu(TCNQ)₂,

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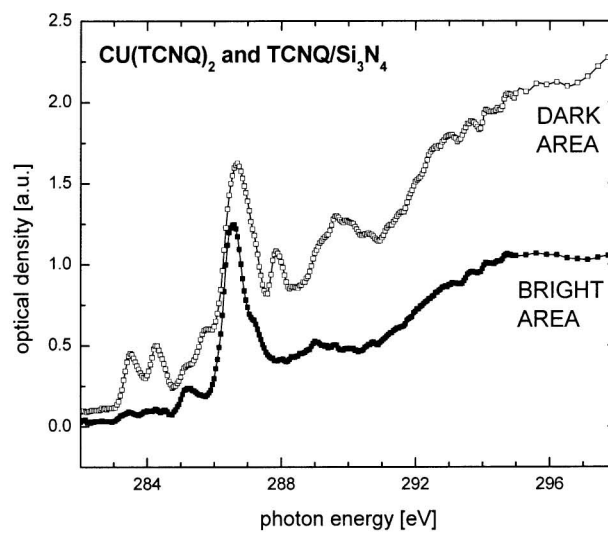
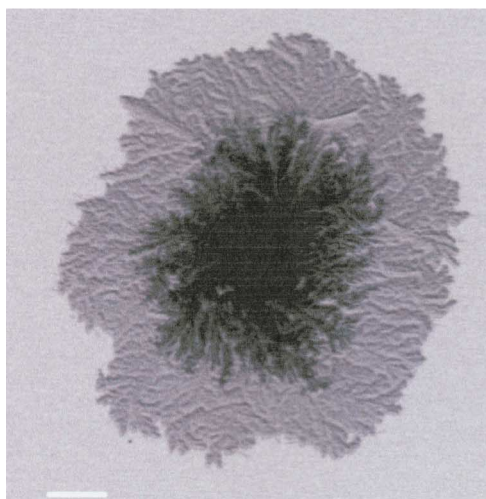


Figure 3: Left: STXM image of Cu(TCNQ)₂ recorded at 288 eV (image size 45 x 45 μm , bar scale 5 μm). Right: Spectra extracted from an image sequence analysis from the bright and dark areas reveal differently oriented crystallites.

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whereas the darker areas consist of unreacted TCNQ. The unreacted TCNQ most likely segregates to the surface, leaving the charge transfer salt underneath. A comparison of the absorption spectra with those recorded from TCNQ and TCNQ-based charge-transfer complexes epitaxially grown on metal substrates [9] indicates that the molecular plane is coplanar with the substrate in the brighter areas that correspond to the charge-transfer complex. In contrast, in the darker areas (unreacted TCNQ), the molecules are likely to be oriented upright. The latter would be the favorable configuration of an OFET. These NEXAFS microscopy results provide guidance on how to optimize the film growth for potential device application.

Additional applications. Some additional applications with the Polymer STXM are: i) imaging of the nanostructure of blockcopolymers [10]; ii) quantifying the distribution of carbon black and other dispersed phases in complex composites [11]; iii) quantitative chemical mapping of “onion-like” polymer nano-structures [12]; iv) linear dichroism studies of nano-crystals of urethane/urea model compounds [13] and alkanes [14]; and vi) several projects of interest to Dow Chemical. In addition, studies of the biochemistry, taxonomy and metal accumulation in biofilms with the Polymer STXM is a major research focus of a collaboration between the Hitchcock group and John Lawrence and Gary Leppard of the National Water Research Institute of

Canada [15]. Biofilm characterization with STXM is highlighted in the article focusing on the ALS BL11.0 STXM [5].

Conclusion

The Polymer STXM at the ALS is now operating and a number of academic and industrial projects are underway. The use of a bending magnet beamline for a STXM resulted in interesting trade-offs. The costs are low enough that the Polymer STXM is a dedicated facility and hence more instrument time than on shared undulator sources is available. At the same time, the performance is still excellent and more than sufficient to characterize samples, particularly organic materials. We have shown a small number of applications to illus-

trate the capabilities of the Polymer STXM. Applications that require polarization control, use of photons outside the 250–600 eV energy range, and very high energy resolution will greatly benefit using the sister-STXM at ALS BL.11.0 that will have user operations soon. ■

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